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(54) Name of the invention:

Photosensitive Paste

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(71) Patent Assignee: Toray Company

## **JP Hei-Sei 9-218509**

*[Note: Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.]*

### **(54) [Name of the Invention]**

Photosensitive Paste

### **(57) [Abstract]**

#### **[Goal]**

The goal of the present invention is to suggest the stabilization of photosensitive paste that enables a high aspect ratio and also high precision patterning technological process.

#### **[Solution Means]**

The solution means is a photosensitive paste characterized by the fact that it contains small (fine) inorganic particles, photosensitive organic compound and a phosphorus-containing compound.

#### **[Scope of the Claims]**

##### **[Claim 1]**

Photosensitive paste characterized by the fact that it contains small inorganic particles, photosensitive organic compound and a phosphorus-containing compound.

##### **[Claim 2]**

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that the phosphorus containing compound is contained in the paste in an amount within the range of 0.01 ~ 10 weight %.

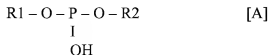
##### **[Claim 3]**

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that as the phosphorus-containing compound a compound that has a P-OH structure in its molecule, is used.

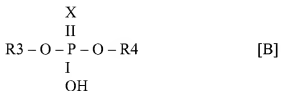
[Claim 4]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that as the phosphorus containing compound a compound that is represented according to the shown below general formulac (A) ~ (C), is used.

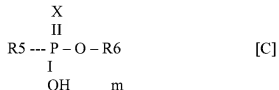
[Formula 1]



[Formula 2]



[Formula 3]



(Where R1 ~ R6: represent hydrocarbon radicals where the number of the carbon atoms is 1 ~ 10, and which contain 0 ~ 4 oxygen atoms, X: represents an oxygen atom or a sulfur atom, m: an integer number 1 ~ 4)

[Claim 5]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that inorganic fine particles are used whose surface is surface treated and covered using phosphorus containing compound.

[Claim 6]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that in the fine inorganic particles at least 50 weight % or more are fine glass particles.

[Claim 7]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles with a glass transition point (T<sub>g</sub>) in the range of 350 ~ 600°C, are used.

[Claim 8]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles with an average refractive index in the range of 1.50 ~ 1.65, are used.

[Claim 9]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles containing bismuth oxide or lead oxide in an amount in the range of 10 ~ 50 weight %, are used.

[Claim 10]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles containing alkali metal oxide in an amount in the range of 3 ~ 20 weight %, are used.

[Claim 11]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles containing the following components, calculated and presented as oxide content, are used.

SiO <sub>2</sub>	5 ~ 50 weight %
B <sub>2</sub> O <sub>3</sub>	5 ~ 50 weight %
BaO	1 ~ 25 weight %
Al <sub>2</sub> O <sub>3</sub>	1 ~ 10 weight %

[Claim 12]

Photosensitive paste according to the above Claim paragraph 6 characterized by the fact that as the fine glass particles fine glass particles where the average particle diameter is within the range of 1 ~ 10 microns, are used

[Claim 13]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that as the photosensitive organic component, carboxylic radical containing polymer material with a weight average molecular weight in the range of 300 ~ 100,000, is used.

[Claim 14]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that as the photosensitive organic component, a C=C double bond containing polymer material with a weight average molecular weight in the range of 300 ~ 100,000, is used.

[Claim 15]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that it contains an ultraviolet light absorbing agent that is comprised of an organic dye material, in an amount in the range of 0.05 ~ 5 weight %.

[Claim 16]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that it is used in plasma displays or plasma address liquid crystal displays.

[Claim 17]

Photosensitive paste according to the above Claim paragraph 1 characterized by the fact that it is used in the formation of the partitioning walls in plasma displays or plasma address liquid crystal displays.

#### **[Detailed Explanation of the Invention]**

[0001]

#### **[Technological Field of the Invention]**

The present invention is an invention about a novel photosensitive paste. The photosensitive paste according to the present invention can be used in plasma displays, plasma address liquid crystal displays, etc., different types of displays, in circuit board material etc., patterning technological processes.

[0002]

In recent years, for the circuit board materials or displays etc., the trend towards small form factor and increase in the precision etc., has continued, and together with that technological advances in the area of the patterning technological processes are desirable. Especially, in the formation of the partitioning walls in the green sheets or plasma display panels that are used in computer CPU etc., materials that have a high degree of precision and also together with that allow for a high aspect ratio patterning technological process, are desirable.

[0003]

In the past, in the case when an inorganic material patterning technological process is conducted, the screen-printing process using a paste formed from inorganic powder material and an organic binder has been widely used. However, in the case of the screen-printing process there has been the drawback point that it is not possible to form a pattern with a high degree of precision.

[0004]

As a method to improve this problem, according to the descriptions reported in the Japanese Patent Application Laid Open Number Hei-Sei 1-296534, Japanese Patent Application Laid Open Number Hei-Sei 2-165538, Japanese Patent Application Laid Open Number Hei-Sei 5-342992, the method of the photolithography technology formation using a photosensitive paste, has been suggested. However, because of the fact that the photosensitive paste has a low degree of sensitivity and image resolution, partition walls with a high aspect ratio and a high precision cannot be obtained, and because of that, for example in the case of the patterning technological process of material where the thickness exceeds 80 microns, it is necessary that a multiple cycle processing technological process (screen printing – light exposure – developing) be conducted, and because of that there has been the drawback point that the process becomes poor.

[0005]

Also, according to the description reported in Japanese Patent Application Laid Open Number Hei-Sei 2-165538, the method has been reported where a photosensitive paste is coated on a transfer paper and after that the transfer film is transferred onto a glass substrate plate and a partitioning wall is formed, and according to the description reported in the Japanese Patent Application Laid Open Number Hei-Sei 3-57138, the method has been reported, correspondingly, where a dielectric material paste is filled in the grooves of a photoresistor layer and the partitioning walls are formed. Also, according to the description reported in the Japanese Patent Application Laid Open Number Hei-Sei 4-109536, the method has been suggested where partitioning walls are formed by using a photosensitive organic film. However, according to these methods there has been the problem that it can be said that the number of the processes is increased since it is necessary to have a transfer film, or a photoresistor or an organic film material. Also, these methods have not reached to the preparation of partitioning walls that have a high degree of precision and a high aspect ratio.

[0006]

#### **[Problems Solved by the Present Invention]**

The authors of the present invention have conducted rigorous research regarding a photosensitive paste that allows a high aspect ratio and also a high precision level patterning technological process, however, there have been cases where depending on the type of the fine inorganic particles used, gelation develops through the reaction with

organic components, and because of the ensuing increase of the viscosity of the paste it has not been possible to use it.

[0007]

The present invention is an invention according to which the gellation of such photosensitive paste is suppressed (controlled) and it is possible to stabilize and use it, thereby producing a paste that enables a high aspect ratio and also high precision degree patterning technological process.

[0008]

#### **[Measures in Order to Solve the Problem]**

The goal of the present invention is achieved through a photosensitive paste where fine inorganic particles and a photosensitive compound containing organic component are used as the main components, and where a phosphorus compound is incorporated into the photosensitive paste.

[0009]

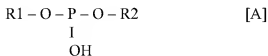
#### **[Conditions of the Practical Embodiment of the Present Invention]**

The phosphorus containing compound that is used according to the present invention is a compound where the phosphorus content in the molecule is in the range of 5 ~ 80 weight %, and by the addition of this phosphorus containing compound in the paste, it is possible to obtain a photosensitive paste with a long pot life. It is also effective if the phosphorus-containing compound is a compound that contains a P - OH radical in its molecule.

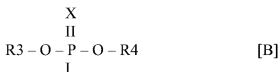
[0010]

Especially, the compound represented according to the general formulae (A), (B), (C),

[Formula 4]

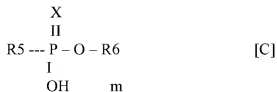


[Formula 5]



OH

[Formula 6]



(Where R1 ~ R6: represent hydrocarbon radicals where the number of the carbon atoms is 1 ~ 10, and which contain 0 ~ 4 oxygen atoms, X: represents an oxygen atom or a sulfur atom, m: an integer number 1 ~ 4), are preferred, and as detailed examples, the following here below compounds can be used.

[0011]

Dibutyl ester of the phosphorous acid (dibutyl phosphite), dimethyl phosphite, methyl phosphite, di propyl phosphite, diphenyl phosphite, phenyl phosphite, isopropyl phosphite, diisopropyl phosphite, n butyl – 2 – ethyl hexyl phosphite, etc., mono alkyl (C 1 ~ 10) esters of the phosphorous acid, dialkyl (C 1 ~ 10) ester of the phosphorous acid, dibutyl phosphate, butyl phosphate, dimethyl phosphate, methyl phosphate, propyl phosphate, di propyl phosphate, diphenyl phosphate, phenyl phosphate, isopropyl phosphate, diisopropyl phosphate, n- butyl – 2- ethyl hexyl phosphate, etc., mono alkyl (C 1 ~ 10) esters of the phosphoric acid, di alkyl (C 1 ~ 10) esters of the phosphoric acid, alkyl esters of the phosphated aliphatic monocarboxylic acids type compounds, thio phosphoric type acid type compounds where the oxygen atom in the above described phosphoric acid esters has been substituted with a sulfur atom, etc., can be listed. Also, it is a good option if compounds are used, where in the alkyl part of the alkyl ester phosphite or the alkyl ester phosphates, acrylic radical, or methacrylic radical, vinyl radical, etc., unsaturated radicals, are contained. Then, it is also a good option to use compounds that contain a phosphonic acid radical or a phosphinic acid radical containing compounds.

[0012]

The higher the ratio of the P – OH bond in the molecule, the more it is possible to increase the effect of preventing the gellation, and because of that, it is preferred to use compounds where the phosphorus content in the molecule is at least 5 weight % or higher.

[0013]

As even more preferable compounds, it is possible to use alkyl diphosphonic acid etc., represented by hydroxy ethylilene diphosphonic acid, or compounds containing 2 or more of the phosphoric acid radicals or phosphorous acid radicals, within the molecule.



[0014]

Regarding the added amount of these phosphorus compounds, by containing them in the paste in an amount that is within the range of 0.01 ~ 10 weight %, and more preferably, within the range of 0.05 ~ 1 weight %, it is possible to obtain a good paste material with a small effect on the photosensitivity properties and on the adhesive properties relative to the substrate plate surface.

[0015]

As the method of addition, it is possible to use the following methods: the method where it is dissolved in the paste, the method where it is dissolved in a solvent agent and after that it is mixed with the paste, the method where it is used to conduct a treatment of the surface of the inorganic particles like fine glass particles, etc. Regarding a more detailed method for the application of the method where a surface treatment is conducted, it is possible to use the method where a phosphorus compound is dissolved in organic solvent medium, or water, etc., liquid material and after that the solvent is evaporated.

[0016]

As the solvent medium, the use of methyl acetate, ethyl acetate, methanol, ethanol, is desirable. It is also preferred that the solvent be evaporated and after that a heat treatment be conducted at a temperature that is in the range of 50 ~ 200°C for a period of 12 hours or more.

[0017]

Regarding the photosensitive paste according to the present invention, it is preferred that it be a paste that contains at least 50 weight % or more of fine, inorganic particles that have been surface treated by using the above described phosphorus type compound.

[0018]

As the fine inorganic particles used according to the present invention, usually, there are the fine particles that can be used in the electronic type materials: glass or metal (gold, platinum, silver, copper, nickel, aluminum, palladium, tungsten, ruthenium oxide etc.), and the particles that are especially effective in the present invention are the fine glass particles. It is preferred that a material be used that contains at least 50 weight % or more of fine glass particles.

[0019]

As the fine glass particles, there are no particular limitations as long as they are the well known materials, however it is preferred to use the glass material that has the following composition:

SiO <sub>2</sub>	5 ~ 50 weight %
B <sub>2</sub> O <sub>3</sub>	5 ~ 50 weight %
BaO	1 ~ 25 weight %
Al <sub>2</sub> O <sub>3</sub>	1 ~ 10 weight %

[0020]

Also, it is also possible that in the glass powder material, TiO<sub>2</sub>, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, etc., be contained, however, it is preferred that its amount be within the range of 0 ~ 20 weight %.

[0021]

For the SiO<sub>2</sub> that is contained in the glass powder material as a component of its composition, it is preferred that it be compounded in an amount that is in the range of 3 ~ 60 weight %. And in the case when that compounded amount is less than 3 weight %, the accurateness properties, the strength and the stability of the glass layer are reduced, and also, there is a mismatch relative to the thermal expansion coefficient of the glass substrate material, and because of that it is outside of the desired values. Also, in the case when the amount compounded is less than 60 weight %, by that the glass transition point becomes low and there is the benefit that it becomes possible to anneal and attach to a glass substrate plate.

[0022]

The B<sub>2</sub>O<sub>3</sub> is compounded in an amount that is within the range of 3 ~ 60 weight %, and by that it is possible to improve the electrical insulation properties, strength, thermal expansion coefficient, insulation layer accurateness, etc., electrical, mechanical and thermal properties. Also, if 60 weight % are exceeded the glass stability properties are decreased.

[0023]

By the addition of BaO and Al<sub>2</sub>O<sub>3</sub>, it is possible to obtain a stabilized glass powder.

[0024]

It is preferred that the ZnO is compounded in an amount of 30 weight % or less. If the compounded amount exceeds 30 weight %, the temperature of the annealing and adhesion to the glass substrate plate becomes too low and it cannot be controlled, and also, the insulation resistance is decreased and because of that it is not preferred.

[0025]

Regarding the diameter of the glass powder particles that are used in the above described, it can be selected depending on the shape of the pattern to be produced, however, it is preferred that 50 weight % of the particles have a diameter within the range of 0.1 ~ 10 microns.

[0026]

Also, the authors of the present invention have observed that by using as the fine glass particles fine glass particles with a spherical shape, the patterning of a high aspect ratio becomes possible.

[0027]

As the fine glass particles that are used in this case, it is appropriate to use glass particles where 50 weight % of the particles have a diameter that is within the range of 1.0 ~ 7 microns, 10 weight % of the particles have a diameter that is within the range of 0.4 ~ 2 microns, and 90 weight % of the particles have a diameter that is within the range of 4 ~ 10 microns, and where the specific surface area is within the range of 0.2 ~ 3.0 m<sup>2</sup>/g. Then, it is preferred that at least 50 weight % or more of fine glass particles are used where the spherical shape coefficient numerical value is at least 80 or higher. Regarding the spherical shape coefficient of the fine glass particles, it is evaluated as the particles are observed by using an electron microscope and it is the ratio representing the number of spherically shaped particles (including also ellipsoid spheres or egg shape spheres).

[0028]

Regarding the glass transition temperature (T<sub>g</sub>) of the fine glass particles used in the case when a patterning technological process on glass substrate plate is conducted, it is preferred that it be within the range of 350 ~ 600°C. For the glass powder material that has such thermal properties, it can be obtained by the incorporation of lead oxide, bismuth oxide, alkali metal oxide etc., and in the case when such components are contained the present invention is especially effective.

[0029]

By having the total content of Bi<sub>2</sub>O<sub>3</sub>, PbO be within the range of 10 ~ 50 weight %, there is the merit point that it becomes easy to control the thermal properties.

[0030]

Also, it is also a good option if Na<sub>2</sub>O, Li<sub>2</sub>O, K<sub>2</sub>O etc., metal oxides are added, however, from the point of view of the water resistant properties it is preferred that the addition is in an amount of 20 weight % or less. However, by the addition of this alkali metal oxide in an amount in the range of 3 ~ 15 weight %, it is a benefit from the point of view that the control of the softening point temperature, the refractive index, the thermal expansion coefficient becomes easy.

[0031]

By having the total amount of the contained  $\text{Bi}_2\text{O}_3$  be within the range of 5 ~ 25 weight %, and also, containing an alkali metal oxide in an amount in the range of 3 ~ 10 weight %, it is possible to obtain glass material with excellent softening temperature, refractive index, thermal coefficient of expansion, electrical stability properties. In the case of such glass, according to the present invention, it becomes possible to use it in photosensitive paste, even though according to the previous technology that has not been used in photosensitive paste because of the easy occurrence of gellation.

[0032]

Also, as the glass powder material, a material is used that has a refractive index in the range of 1.50 ~ 1.65 at the mercury lamp g rays (436 nm), and by that it is possible to adjust to the refractive index of the organic component, and through the control of the light diffusion, a high precision level patterning technological process becomes possible.

[0033]

As the photosensitive organic component used according to the present invention, it is the organic component containing the compound that possesses the photosensitive properties in the paste (the part of the paste with the exception of the inorganic component).

[0034]

In the photosensitive organic component, there is a reactive component that is selected from at least one type of photosensitive monomer material, photosensitive oligomer material, photosensitive polymer material, and a binder, a photo polymerization initiation agent, an ultraviolet light absorbing agent, a sensibilization aid agent, a polymerization termination agent, plasticising agent, organic solvent medium, anti-oxidation agent, dispersing agent, organic or inorganic anti-settling agent, etc., additive components can also be added.

[0035]

Regarding the photosensitive paste material that is used according to the present invention, from the point of view of the degree of sensitivity relative to the light, it is preferred that it be a paste material where the content of the organic component be at least 10 weight % or higher in the photosensitive organic components. Then, it is preferred that it be a material where that content is at least 30 weight % or higher.

[0036]

As the reactive component, there are light non-dissolving type materials and light dissolving type materials. As the light non-dissolving type materials, there are the

following materials: (1) materials containing functional properties possessing monomers, oligomers, polymers where at least one or more unsaturated radicals are contained in the molecule; (2) materials containing photosensitive properties possessing compound, like aromatic diazo type compounds, aromatic azide type compounds, organic halogenated type compounds, etc.; (3) materials called diazo resins that are obtained as condensation materials from diazo type amine and formaldehyde, etc. Also, as the light dissolving type materials, there are the following materials: (4) materials containing complex compounds obtained from diazo compound and inorganic salt or organic acid, quinone diazo type etc.; (5) materials where a quinone diazo type compound and an appropriate polymer binder are bonded, for example, phenol, Novolac resin naphthoquinone 1, 2 – diazide – 5 – sulfonic acid ester, etc.

[0037]

Regarding the reactive component that is used according to the present invention, it is possible to use all of the above-described materials, however, the materials described in (1) are the simplest photosensitive paste.

[0038]

As the reactive monomers that are used in this case, they are compounds containing a double C=C bond, and as detailed examples of these compounds it is possible to list the following materials: methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-pentyl acrylate, allyl acrylate, benzyl acrylate, butoxy ethyl acrylate, butoxy triethylene glycol acrylate, cyclo hexyl acrylate, dicyclo pentanyl acrylate, dicyclo pentenyl acrylate, 2-ethyl hexyl acrylate, glycerol acrylate, glycidyl acrylate, hepta decyl fluoro decyl acrylate, 2-hydroxy ethyl acrylate, iso bonyl acrylate, 2-hydroxy propyl acrylate, iso decyl acrylate, iso octyl acrylate, lauryl acrylate, 2-methoxy ethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene glycol acrylate, octa fluoro pentyl acrylate, phenoxy ethyl acrylate, stearyl acrylate, trifluoro ethyl acrylate, allylated cyclo hexyl diacrylate, 1, 4 – butane diol diacrylate, 1, 3 – butylenes glycol diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol diacrylate, dipenta erithritol hexa acrylate, dipenta erithritol monohydroxy penta acrylate, di trimethylol propane tetra acrylate, glycerol diacrylate, methoxylated cyclo hexyl diacrylate, neopentyl glycol diacrylate, propylene glycol diacrylate, polypropylene glycol diacrylate, triglycerol diacrylate, trimethylol propane triacrylate, acrylamide, amino ethyl acrylate, and materials where one part or all of the acrylate in the molecules of the above described compounds is substituted with methacrylate,  $\gamma$  – methacryloxy propyl trimethoxy silane, 1-vinyl – 2 – pyrrolidone etc.

[0039]

According to the present invention it is possible to use one type or two or more types of these materials. Besides the above-described materials, by the addition of unsaturated carboxylic acids it is possible to improve the developing processing properties in the

developing process that is conducted after the light sensitive process. As detailed examples of the unsaturated carboxylic acids it is possible to list the following: acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, or their acid anhydrides, etc.

[0040]

On the other hand, as photosensitive properties possessing oligomers or polymers, it is possible to use oligomers or polymers that are polymerized by using the above described reactive monomers and benzene ring, naphthalene ring, etc., aromatic ring containing methacrylate monomers or acrylate monomers, in more details, phenyl (meth) acrylate, phenoxy ethyl (meth) acrylate, benzyl (meth) acrylate, 1-naphthyl (meth) acrylate, 2-naphthyl (meth) acrylate, bis phenol A di (meth) acrylate, bis phenol A ethylene oxide adduct material di (meth) acrylate, bis phenol A propylene oxide adduct material di (meth) acrylate, thio phenol (meth) acrylate, benzyl mercaptane (meth) acrylate, and also monomers where among the hydrogen of these benzene rings, 1 ~ 5 are substituted with chlorine or bromine atoms, or it is possible to use oligomers or polymers that are obtained by the polymerization of at least one type or more of styrene, p-methyl styrene, o-methyl styrene, m-methyl styrene, chlorinated styrene, brominated styrene,  $\alpha$ -methyl styrene, chlorinated  $\alpha$ -methyl styrene, brominated  $\alpha$ -methyl styrene, chloro methyl styrene, hydroxy methyl styrene.

[0041]

At the time of the polymerization, it can be conducted as the content of these monomers is made to be at least 10 weight % or higher, and then preferably, it is made to be at least 35 weight % or higher, and it is copolymerized with the other reactive monomers. As the copolymerized monomers, it is possible to use the above described compounds containing the unsaturated double C=C bond.

[0042]

Also, by the copolymerization of unsaturated carboxylic acid it is possible to improve the developing properties of the developing process that is conducted after the light sensitive process. As detailed examples of the unsaturated carboxylic acids there are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, or their acid anhydrides, etc. Especially, the present invention is effective in the case when a carboxylic radical containing polymer is used in the organic component.

[0043]

Regarding the acid value (AV) of the obtained by this polymer or oligomer material that contains a carboxylic radical in its side chain, it is within the range of 50 ~ 180, and preferably, it is within the range of 70 ~ 140. In the case when the acid value is less than 50, or when it exceeds 180, the window allowing the developing becomes narrow, and it is difficult to obtain a high precision patterning.

[0044]

Relative to the above described polymers or oligomers, by the addition of photo reactive radical in the side chain or at the ends of the molecule it is possible to impart photosensitive properties. The preferred photosensitive radicals are those containing ethylenic unsaturated radicals. As ethylenic unsaturated radicals, there are the vinyl radical, the allyl radical, the acrylic radical, the methacrylic radical, etc.

[0045]

Regarding the method of the addition of such side chain to the oligomer or the polymer, it is possible to use the method where an adduct reaction is produced of the addition of glycidyl radical or isocyanate radical containing ethylenic unsaturated compounds or of chloride acrylate, chloride methacrylate, or allyl chloride relative to the mercapto radical, amino radical, hydroxyl radical or carboxylic radical in the polymer.

[0046]

As the glycidyl radical containing ethylenic unsaturated compounds, there are the following compounds: glycidyl acrylate, glycidyl methacrylate, acryl glycidyl ether, glycidyl ethyl acrylate, crotonyl glycidyl ether, glycidyl ether crotonate, glycidyl ether isocrotonate etc.

[0047]

As the isocyanate radical containing ethylenic unsaturated compounds, there are the (meth) acryloyl isocyanate, (meth) acryloyl ethyl isocyanate, etc. Also, it is preferred that the equivalent amount added of the glycidyl radical or isocyanate radical containing ethylenic unsaturated compounds, or of the chloride acrylate, chloride methacrylate or allyl chloride relative to the mercapto radical, the amino radical, the hydroxyl radical or the carboxylic radical in the polymer, be within the range of 0.05 ~ 1 mole.

[0048]

In the photosensitive paste according to the present invention it is also possible that binders, photo polymerization initiation agent, ultraviolet light absorbing agent, sensibilization agent, sensibilization aid agent, polymerization termination agent, plasticising agent, thickening agent, organic solvent media, anti-oxidation agent, dispersing agent, organic or inorganic anti-settling agent, etc., additive agent components are also added.

[0049]

As the binder material, it is possible to list polyvinyl alcohol, polyvinyl butyral, methacrylic acid ester polymer materials, acrylic acid ester polymer materials, acrylic

acid ester – methacrylic acid ester copolymer materials,  $\alpha$ -methyl styrene polymer materials, butyl methacrylate resins etc.

[0050]

As detailed examples of the materials used as photo polymerization initiation agents, it is possible to list the following materials: benzophenone, o-benzoyl methyl benzoate, 4, 4 – bis (dimethylamine) benzophenone, 4, 4 – bis (diethylamine) benzophenone, 4, 4 – dichloro benzophenone, 4- benzoyl – 4 – methyl diphenyl ketone, dibenzoyl ketone, fluorenone, 2, 2 – diethoxy acetophenone, 2, 2 – dimethoxy – 2- phenyl – 2 – phenyl acetophenone, 2 – hydroxy – 2 – methyl propio phenone, p – t – butyl dichloro acetophenone, thioxantone, 2-methyl thioxantone, 2-chloro thioxantane, 2-isopropyl thioxantone, diethyl thioxantone, benzyl, benzyl dimethyl ketanole, benzyl – 2 – methoxy ethyl acetal, benzoin, benzoin methyl ether, benzoin butyl ether, anthraquinone, 2 – t – butyl anthraquinone, 2-amyl anthraquinone,  $\beta$ -chloranthraquinone, antrone, benzantrone, dibenzosperone, methylene antrone, 4-azide benzal acetophenone, 2, 6 – bis (p-azide benzylidene) cyclo hexanone, 2, 6 – bis (p-azide benzylidene) – 4 – methyl cyclo hexanone, 2 – phenyl – 1, 2 – butadiene – 2 – (o-methoxy carbonyl) oxime, 1-phenyl – propane dione – 2 – (o-ethoxy carbonyl) oxime, 1, 3 – diphenyl – propane trione – 2 – (o-ethoxy carbonyl) oxime, 1- phenyl – 3 – ethoxy – propane trione – 2 – (o-benzoyl) oxime, mihira – ketone, 2-methyl – [4 – (methylthio) phenyl] – 2 – morpholine – 1 – propanone, naphthalene sulfonyl chloride, quinoline sulfonyl chloride, N-phenyl thioacrydon, 4, 4 – azo bis isobutyronitrile, diphenyl disulfide, benzthiazol disulfide, triphenyl morphin, camphor quinone, carbon tetra bromide, tribromo phenyl sulfon, benzoin peroxide, and eosin, methylene blue, etc., photo-reductive properties possessing dyes and ascorbic acid, triethanolamine etc., reductive agents combinations, etc. According to the present invention it is possible to use one type or two or more types of these materials. Regarding the photo polymerization initiation agents, relative to the reactive components, they can be added in an amount that is within the range of 0.05 ~ 10 weight %, and more preferably, it is within the range of 0.1 ~ 5 weight %. If the amount of the photo polymerization initiation agent is too small, the photosensitivity degree becomes poor, and if the amount of the photo polymerization initiation agent becomes too high, there is the danger that the retention ratio of the light exposure part would become too small.

[0051]

IT is also effective if an ultraviolet light-absorbing agent, which is comprised of an organic dye material, is added. By the addition of a light-absorbing agent that has a high ultraviolet light absorbing effect, it is possible to obtain a high aspect ratio, high level of precision and high image resolution. As the ultraviolet light absorbing agent, it is possible to use materials formed from organic type dyes, and among those, the organic dye materials that have a high UV absorption coefficient in the 350 ~ 450 nm wavelength range, are preferably used. In more details, it is possible to use azo type dye materials, amino ketone type dye materials, xantene type dye materials, quinoline type dye materials, amino ketone dye materials (this is a repeat of the above? – translator's note), anthraquinone type, benzophenone type, diphenyl cyano acrylate type, triazine type, p-



amino benzoic acid type dye materials, etc. Even in the case when an organic dye material is added as a light absorbing agent, it is preferred that it does not remain in the insulation layer after the sintering, in order to minimize as much as possible the decrease of the properties of the insulation layer due to the light absorbing agent. Even among these, the azo type and the benzophenone type dye materials are preferred. It is preferred that the added amount of the organic dye materials is within the range of 0.05 ~ 5 weight parts. In the case when this amount is less than 0.05 weight %, the effect of the addition of the ultraviolet light absorbing agent is decreased, and in the case when the added amount exceeds 5 weight %, the properties of the insulation layer after the sintering, are decreased, and that is why these options are not preferred. More preferably, the added amount is within the range of 0.15 ~ 1 weight %. If we are to present one example of the method of the addition of the ultraviolet light absorbing agent that is comprised of an organic dye material, it is possible to be done according to the following: the organic dye material is in advance dissolved in organic solvent medium and a solution is produced and after that in the above organic solution a glass powder material is admixed and after that it is dried. According to this method, it is desirable that an organic layer is coated on the powder surface of each individual glass powder particle, and by that it is possible to manufacture the so-called capsule type powder material.

[0052]

The sensibilization agent is added in order to increase the sensitivity degree. As detailed examples of the sensibilization agent it is possible to list the following here below materials: 2, 4 - diethyl thioxantone, isopropyl thioxantone, 2, 3 - bis (4-diethyl amino benzal) cyclo pentanone, 2, 6 - bis (4 -dimethyl amini benzal) cyclo hexanone, 2, 6 - bis (4- dimethyl amino benzal) - 4 - methyl cyclo hexanone, mihira ketone, 4, 4 - bis (diethyl amino) - benzophenone, 4, 4 - bis (dimethyl amino) carbon, 4, 4 - bis (diethyl amino) carbon, p- dimethyl amino cinnamylidene idanone, p-dimethyl amino benzylidene indanone, 2 - (p-dimethyl amino phenyl vinylene) - isonaphtho thiazol, 1, 3 - bis (4 - dimethyl amino benzal) acetone, 1, 3 - carbonyl - bis (4-diethyl amino benzal) acetone, 3, 3 - carbonyl - bis ( 7-diethyl amino cumaron), N - phenyl - N - ethyl ethanolamine, N - phenyl ethanolamine, N-tolyl diethanolamine, N- phenyl ethanolamine (the same as above? - translator's note), isoamyl dimethyl amino benzoate, isoamyl diethyl amino benzoate, 3 - phenyl - 5- benzoyl thio tetrazole, 1 - phenyl - 5 - ethoxy carbonyl thio - tetrazole, etc. According to the present invention it is possible to use one type or two or more types of these. Moreover, it is also possible to use materials among the sensibilization agents as photo polymerization initiation agents. In the case when a sensibilization agent is added into the photosensitive paste according to the present invention, its added amount is usually in the range of 0.05 ~ 5 weight %, relative to the reactive component, and preferably, it is within the range of 0.1 ~ 2 weight %. If the amount of the sensibilization agent is smaller than that, there is no demonstration of the effect of the increasing of the degree of light sensitivity, and if the amount f the sensibilization agent is too high, there is the danger that the retention ratio of the light exposure part would become too small.

[0053]

Regarding the polymerization termination agent, it is added in order to increase the thermal stability properties at the time of the storage. As detailed examples of the polymerization termination agent it is possible to list the following here below materials: hydroquinone, monoesterified material of the hydroquinone, N-nitron diphenyl amine, pheno thiazine, p - t - butyl catechol, N-phenyl naphthylamine, 2, 6 - di - t - butyl - p - methyl phenol, chloranyl, pyrogallol, etc. In the case when a polymerization termination agent is added its amount is usually in the range of 0.001 ~ 1 weight % in the photosensitive paste.

[0054]

As detailed examples of the plasticising agent, it is possible to list dibutyl phthalate, dioctyl phthalate, polyethylene glycol, glycerin etc.

[0055]

Regarding the anti-oxidation agent it is added in order to prevent the oxidation of the acrylic type polymer material at the time of the storage. As detailed examples of the anti-oxidation agents, it is possible to list the following materials: 2, 6 - di - t - butyl - p - cresol, butylated hydroxy anisol, 2, 6 - di - t - 4 - ethyl phenol, 2, 2 - methylene - bis - (4 - methyl - 6 - t - butyl phenol), 2, 2 - methylene - bis - (4-ethyl - 6 - t - butyl phenol), 4, 4' - bis - (3-methyl - 6 - t - butyl phenol), 1, 1, 3 - tris - (2 - methyl - 6 - t - butyl phenol), 1, 1, 3 - tris - (2 - methyl - 4 - hydroxy - t - butyl phenyl) butane, bis [3, 3 - bis - (4-hydroxy - 3 - t - butyl phenyl) butyric acid] glycol ester, dilauryl thio dipropionate, triphenyl phosphite, etc. In the case when an anti-oxidation agent is added, the added amount is usually in the range of 0.001 ~ 1 weight % in the paste.

[0056]

In the case when it is desired to adjust the viscosity of the solution, it is also a good option if an organic solvent medium is added in the photosensitive paste according to the present invention. As the organic solvent medium that is used at that time, it is possible to use methyl cellosolf, ethyl cellosolf, butyl cellosolf, methyl ethyl ketone, dioxane, acetone, cyclohexanone, cyclopentanone, isobutyl alcohol, isopropyl alcohol, tetrahydrofuran, dimethyl sulfoxide,  $\gamma$ -butyrolactone, bromobenzene, chlorobenzene, dibromobenzene, bromobenzoate, chloro benzoate, etc., and it is possible to use one type or to use two or more types of these as a mixed organic solvent medium.

[0057]

At the time when the paste is produced there is the problem that it is said that the metal oxide of the fine glass particles reacts with the organic component and the viscosity is increased, and in order to prevent that it is desirable to add a gellation preventing agent.

[0058]

Usually, the photosensitive paste is produced as fine inorganic particles, ultraviolet light absorbing agent, photosensitive polymer, photosensitive monomer, photo polymerization initiation agent, glass frit and a solvent agent, etc., each type components are mixed and compounded so that the predetermined composition is obtained, and after that this material is homogeneously mixed and kneaded by using three rollers or a mixing/kneading device. The paste viscosity can be appropriately adjusted depending on the addition ratios of the fine inorganic particles, the thickening agent, the organic solvent agent, the plasticizer agent, and the anti-settling agent, etc., however it is preferred that its range be within 200 ~ 200,000 cps (centipoises).

[0059]

After that, an explanation will be provided regarding an example where the photosensitive paste is used and a patterning process is conducted, however the present invention is not limited by that example.

[0060]

On the surface of a glass substrate plate or a ceramics substrate plate the photosensitive paste is coated on the whole surface or on part of it. As the coating method it is possible to use the screen-printing method, the bar coater method, the roll coater method, etc., well known methods. Regarding the coating thickness, it is possible to be appropriately determined by selecting the number of coating cycles, the screen mesh, and the paste viscosity.

[0061]

Here, in the case when the paste is coated on the surface of the glass substrate plate in order to increase the adhesive properties between the substrate plate and the coated layer, it is possible to conduct a surface treatment of the substrate plate. As the surface treatment solution, there are silane coupling agents, for example, vinyl trichloro silane, vinyl trimethoxy silane, vinyl triethoxy silane, tris - (2-methoxy ethoxy) vinyl silane,  $\gamma$  - glycidoxy propyl trimethoxy silane,  $\gamma$  - (methacryloxy propyl) trimethoxy silane,  $\gamma$  (2-aminoethyl) aminopropyl trimethoxy silane,  $\gamma$  - chloropropyl trimethoxy silane,  $\gamma$  - mercaptopropyl trimethoxy silane,  $\gamma$  - aminopropyl triethoxy silane, etc., or organic metal compounds, for example, organo-titanium compound, organo-aluminum compound, organo-zirconium compound, etc. Materials are used that are obtained as the silane coupling agent or the organo-metal compound are diluted to a concentration in the range of 0.1 ~ 5 % by using organic solvent medium like for example, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, etc. After that, this surface treatment solution is homogeneously coated on the surface of the substrate plate by using a spinner device etc., and after that it is dried at a temperature in the range of 80 ~ 140°C for a period of 10 ~ 60 minutes and by that it is possible to conduct the surface treatment.

[0062]

After that on the coated layer, by using a photo mask, a mask light exposure is conducted. The selection of whether the used mask is a negative type or a positive type mask can be made based on the type of the photosensitive organic component used. Regarding the active light source that is used at this time, for example, there are the near ultraviolet light, ultraviolet light, electron beam, X ray etc., however, among these the ultraviolet light is preferred, and as the source for that, for example, low pressure mercury lamp, high pressure mercury lamp, ultra-high pressure mercury lamp, halogen lamp, bactericide lamp, etc., can be used. Among these, the ultra-high pressure mercury lamp is preferred. The conditions of the light exposure vary depending on the coating thickness, however, by using a 5 ~ 100 mW/cm<sup>2</sup> output ultra-high pressure mercury lamp, the light exposure is conducted for a period in the range of 1 ~ 30 minutes.

[0063]

If a photosensitive paste is coated and after that on its surface oxygen barrier layer is provided, by that it is possible to improve the shape of the patterning. As one example of the oxygen barrier layer, it is possible to point out a PVA layer. Regarding the method for the formation of the PVA layer, it is possible to use the method whereby a PVA aqueous solution with a concentration in the range of 0.5 ~ 5 weight % is homogeneously coated on the surface of a substrate plate by using a spinner, and after that it is dried at a temperature in the range of 70 ~ 90°C for a period of 10 ~ 60 minutes. The preferred PVA solution concentration is within the range of 1 ~ 3 weight %. If this concentration is used, the level of the sensitivity is even further increased. It is assumed that the increase in the level of the sensitivity through the PVA coating is because of the following here below reasons. Namely, at the time when the reactive properties possessing component is photo reacted, if there is oxygen in the air atmosphere, it is considered that the photo curing sensitivity is hindered, however, if there is a PVA layer, it is possible to intercept the excess oxygen and because of that the sensitivity level at the time of the light exposure is increased and that is why it is a preferred option. Besides PVA it is also possible to use other water soluble, transparent polymers, for example, it is possible to use cellulose type materials, like methylcellulose etc.

[0064]

After the light exposure, a developing solution is used and developing is conducted, however, in this case, it is conducted by the immersion method or by the spray method. Regarding the developing solution, it is possible to use an organic solvent medium that is capable of dissolving the organic component used in the photosensitive paste. Also, it is possible to add water into the above organic solvent medium as long as it is within the range where its dissolving power is not lost. In the case when a carboxylic radical containing compound is present in the photosensitive paste, it is possible to use alkali water solution as the image developer. As the alkali water solution, it is possible to use aqueous solutions of sodium hydroxide or potassium hydroxide, etc., metal alkali water solutions, however, the use of organic alkali aqueous solution is preferred because of the

fact that it is easy to eliminate the alkali component at the time of the sintering. As the organic alkali, it is possible to use the well-known amine compounds. In more details, it is possible to list tetramethyl ammonium hydroxide, trimethyl benzyl ammonium hydroxide, monoethanol amine, diethanol amine, etc. Regarding the concentration of the alkali aqueous solution, usually, it is within the range of 0.01 ~ 10 weight %, and more preferably, it is within the range of 0.1 ~ 5 weight %. If the alkali concentration is too low, it is not possible to eliminate the unexposed parts, and if the alkali concentration is too high, there is the danger that the pattern part would be separated, or that the light exposure part would be corroded, and that is why these are not preferred options.

[0065]

After that, sintering (annealing) is conducted in an annealing kiln. The ambient atmosphere and the temperature conditions of the annealing vary depending on the type of the paste and the type of the substrate plate, however, usually, the sintering is conducted in an air or nitrogen gas ambient atmosphere. The annealing temperature is within the range of 400 ~ 1000°C. In the case when a patterning technological process is conducted on the surface of a glass substrate plate or in the case when silver is used as the fine inorganic particles, the sintering is conducted as it is maintained at a temperature in the range of 520 ~ 610°C, for a period of 10 ~ 60 minutes.

[0066]

Also, during the above-described technological process, it is also a good option if a technological process of heating at a temperature in the range of 50 ~ 300°C is incorporated in order to conduct drying and preliminary reaction.

[0067]

### **[Practical Examples]**

Here below, the present invention will be explained in further details by using practical implementation examples. However, the present invention is not limited by these examples. Moreover, the concentration (%) in the practical and reference examples denotes weight % concentration.

[0068]

In the case of the practical example implementation, a photosensitive paste formed from fine glass particles and photosensitive organic component, was produced. Regarding the order of the preparation, first, while each component of the photosensitive organic components was heated at a temperature of 80°C, they were melted and after that the inorganic particles were added, and mixed and kneaded by using a mixing/kneading device, and by that the paste material was produced.

[0069]

After that, on a 30 cm square solder glass substrate plate, by using a doctor blade a coating process was conducted so that a thickness of 130 micron was obtained, and after that this was dried at a temperature of 80oC for a period of 30 minutes. However, there was gellation due to the paste and the coating was impossible. Then, evaluation was conducted as to whether or not it is a state allowing coating after 1 day, after 3 days and after 7 days. For the materials where coating was possible, the light exposure and developing were conducted according to the described here below conditions.

[0070]

After that by using a stripe shaped mask used for the partitioning walls utilized in plasma displays etc., a light exposure was conducted. The mask was a chrome mask provided so that it becomes possible to make a stripe shaped pattern where the pitch was 220 microns, the line width was 60 microns. The light exposure was conducted by ultraviolet beam exposure light obtained from an ultra-high mercury lamp with an output of 50 mW/cm<sup>2</sup>.

[0071]

After that, this was immersed in a 1% aqueous solution of mono ethanolamine and the developing was conducted. Then, the obtained glass substrate plate was dried at a temperature of 120oC for a period of 1 hour, and after that the annealing was conducted at a temperature of 560oC for a period of 15 minutes.

[0072]

The evaluation of the patterning process properties was conducted by observation of the pattern shape (line width 50 microns x height 100 microns, pitch 220 microns – target) using an electron microscope.

[0073]

The composition of the photosensitive paste according to this practical implementation example is shown here below.

Fine glass particles	: clarified according to the described below	80 weight parts
Photosensitive monomer: TMPTA		9.0 weight parts
Photosensitive polymer: Polymer – 1		13.3 weight parts
Photo polymerization initiation agent: MTPMP		2.0 weight parts
Ultraviolet light absorbing agent: sudan		0.1 weight parts
Sensibilization agent: DET		2.0 weight parts
Sensibilization aid agent: EPA		1.0 weight parts
Organic solvent medium: $\gamma$ -BL		21.7 weight parts

[0074]

Relative to the notations in the table above, they are according to the described here below.

[0075]

(The numbers and letters in the polymer structure indicate the mole ratio of the corresponding monomer structure)

TMPTA: trimethylol propane triacrylate

Polymer 1:  
[Formula 7]

(Formula shown in the Japanese original on page 10)

MTPMP: 2-methyl – 1 – [4 – (methylthio) phenyl] – 2 morpholino propane – 1

Sudan: Azo type dye, C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O

DET: 2, 4 – diethyl thio xantone

EPA: ethyl ester of the p-dimethylamino benzoic acid

DBP: dibutyl phthalate

γ-BL: γ- butyrolactone

Relative to the anti-gellation agent, according to the Practical Examples 1 ~ 8, it was dissolved in isopropyl alcohol and after that at a temperature of 50°C and under reduced pressure the solvent was evaporated and after that at a temperature of 80°C heating was conducted for a period of 5 hours, and an anti-gellation agent was coated on the fine inorganic particles. According to the Practical Example 9, there was no surface coating, and it was dissolved in the paste and used that way.

[0076]

Within these practical implementation examples, in the case of the Practical Examples 1 ~ 5 and the Reference Example 1, the glass 1 was used, and in the case of the Practical Examples 6 ~ 9 and in the Reference Example 2, the glass 2, was used.

[0077]

**Glass 1**

Bi2O3	:	37 weight %
B2O3	:	14 weight %
SiO2	:	17 weight %
ZnO	:	16 weight %
BaO	:	8 weight %
Al2O3	:	4 weight %
Na2O3	:	4 weight %

Sphericity coefficient 85 %, refractive index 1.73, 50 weight % of the particles have an average particle diameter of 3.2 microns.

**Glass 2**

Bi2O3	:	37 weight %
B2O3	:	14 weight %
SiO2	:	17 weight %
ZnO	:	16 weight %
BaO	:	8 weight %
Al2O3	:	4 weight %
Na2O3	:	4 weight %

Sphericity coefficient 88 %, refractive index 1.58, 50 weight % of the particles have an average particle diameter of 3.3 microns.

**[Table 1]**

	Anti-Gellation Agent	Used Amount	After 3 days	After 7 days	After 14 days
Practical Example 1	DBPO	0.5 %	O	O	Δ
Practical Example 2	DBP	0.2 %	O	Δ	X
Practical Example 3	DBP	0.5 %	O	O	O
Practical Example 4	HEDP	0.1 %	O	O	O
Practical Example 5	HEDP	0.2 %	O	O	O
Practical Example 6	HEDP	0.01 %	O	Δ	Δ
Practical Example 7	HEDP	0.1 %	O	O	O
Practical Example 8	HEDP	0.5 %	O	O	O



Practical Example 9	MEP	3.5 %	O	O	Δ
Reference Example 1	Not used		X	X	O
Reference Example 2	Not used		X	X	X

O: it is a good state of the paste whereby it is possible to obtain a good pattern.

Δ: it is a state of the paste whereby it is possible to coat, however, because of the fact that the developing is not good, a good pattern is not obtained.

X: it is a state of the paste where it cannot be coated.

DBPO: dibutyl phosphate

DBP: dibutyl phosphite

HEDP: hydroxy ethylene diphosphonic acid

MEP: methacryloyl ethyl ester of the phosphoric acid

[0078]

#### **[Results from the Present Invention]**

Through the anti-gellation agent according to the present invention it becomes possible to stably use a photosensitive paste that allows for a high aspect ratio and also high precision level patterning technological process. By that, it becomes possible to achieve a high precision level patterning technological process, to increase the precision properties, and to simplify the technological processes.

[0079]

Especially, it is possible to form by a simple method the high precision level partitioning walls of plasma display panels.

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